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suppressed. Consequently, the exchange must be considerably impeded.

In order to check this theory, we investigated the rate of exchange of ammonium nitrate, ammonium sulfate, and ammonium chloride with heavy water in the presence as well as the absence of the corresponding acids. The experiments were carried out in the following manner. To a weighed-in quantity of the salt dissolved in water or dilute acid a weighed-in quantity of heavy water having a known deuterium content (25% D<sub>2</sub>O) was added. Both liquids had been cooled to the temperature of the experiment. After a set period of time, a portion of salt for analysis of the isotope composition was separated from the solution. We encountered the difficulty that no suitable reaction for the precipitation of the ammonium ion from acidic solutions is known in the course of which the mixture is not diluted by a considerable quantity of ordinary hydrogen. In the majority of experiments, precipitation was carried out by adding an excess of acetone which was dry and had been cooled to the necessary temperature. Control experiments established the complete absence of exchange with acetone under the conditions of our experiments. All operations necessary for the separation of the salt sample by this method took 1/2 to 1 minute.

In several experiments with ammonium nitrate, precipitation of the salt was effected by freezing it out. In view of the fact that this process takes 15 min, the method in question is suitable only for a qualitative ~~determ~~ confirmation of the fact that delayed exchange takes place. Finally, several experiments with precipitation by diisobutyl ether were carried out. This procedure also required several minutes.

The precipitated salt after sucking off was dried in vacuum at 80°. The content of deuterium in it was determined by reverse exchange of a weighed-in quantity of the dried salt with a weighed sample of ordinary water. After completion of the exchange, a part of the water was distilled off and its density measured according to the temperature at which the hydrometer floated.

In tables 1 and 2, the results of several typical experiments on the exchange of ammonium nitrate and ammonium sulfate are cited. These data are not quantitative, because the precipitation took place during some period of time which was not exactly reproducible. During this time, the exchange continued under conditions of concentrations and of a temperature which were variable.

This refers particularly to experiments in which precipitation with acetone was carried out immediately after addition of heavy water and energetic stirring. In these experiments a time of exchange equal to 1 min was arbitrarily assumed. Apparently these sources of error explain a certain quantitative inconsistency in the collation of data that becomes noticeable after the data have been collated. Both tables show, however, that in accordance with theoretical concepts, exchange in the case of the ammonium ion does not proceed instantaneously, but with a measurable velocity, and is strongly impeded in the presence of an excess of free acid that suppresses hydrolysis. The reduction of the rate of exchange is smaller for ammonium sulfate, because the comparatively low solubility of this salt did not permit the use of highly concentrated solutions of sulfuric acid. The solubility of ammonium chloride is still lower, and for that reason experiments with this salt yield qualitative results only. In these experiments, solutions of 0.2 g of salt in 1 g of water at 0° gave 70-80% of exchange in 1 min, while solutions of 0.1 g of salt in 1 g of 1N HCl gave 55-70% of exchange under the same conditions.

The following proximate equation describes the kinetics of exchange proceeding over free ammonia in a system which is in a state of equilibrium with respect to hydrolysis:

$$-\ln(1-x) = 2k W \left(1 + \frac{N}{W+B}\right) t$$

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In this equation,  $\alpha$  is the fraction of exchange with respect to equilibrium,  $k$  is the rate constant of the straight line for the reaction of the hydrolysis of  $\text{NH}_4^+$ , and  $W$ ,  $N$ , and  $B$  concentrations of water, salt, and the added acid respectively. In deriving this equation, we neglected the presence of molecules in which more than one atom of hydrogen is replaced by deuterium, and also the effect of isotopic exchange on the degree of hydrolysis.

While the limits of reproducibility of our data do not permit a quantitative check of this equation, it does without any doubt describe correctly the kinetics of exchange. In particular, this equation explains why in strongly acidic solutions where the concentration of ammonia is reduced by a factor of  $10^3$  with respect to the neutral solution, the rate of exchange is reduced by approximately one order only, although this exchange takes place over free ammonia.

The results of this investigation give added confirmation to the above-mentioned theory of hydrogen exchange in solution, and to the fundamental deduction from this theory that capacity for exchange is determined by the structure of the electronic shell surrounding the atom rather than the nature of the bond X-H.

## Bibliography.

1. A. I. Brodskiy, Izv AN SSSR, OKhN, No 1, p 3 (1949)
2. A. I. Brodskiy and I. G. Khaskin, DAN SSSR, Vol LXXIV, No 2 (1950)

Table 1. Exchange in  $\text{NH}_4\text{NO}_3$ . Acid: 54%  $\text{HNO}_3$ 

temperature C°	time in min	without acid		with acid	
		$\frac{\text{g salt}}{\text{g water}}$	% of exchange $\alpha$	$\frac{\text{g salt}}{\text{g water acid}}$	% of exchange $\alpha$
-10	1			0.36	23
0	1	1.14	76	0.38	36
0	10	1.04	82	0.35	58
20	15	1.11	102		
0	15*			0.41	59
0	2**			0.37	64
0	35**			0.25	90

\* Precipitation by freezing out; 1/3% acid. Precipitation continued for 15 min at -10°.

\*\* Precipitation with dioxane added after expiration of the time indicated in the table. Precipitation continued for 5 min at plus 10 to plus 12°.

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Table 2. Exchange in  $(\text{NH}_4)_2\text{SO}_4$ . Acid: 13%  $\text{H}_2\text{SO}_4$ 

temperature	time in min	without acid		with acid	
		$\frac{\text{g salt}}{\text{g water}}$	% of exchange $\alpha$	$\frac{\text{g salt}}{\text{g water acid}}$	% of exchange $\alpha$
0 0 0	1	0.36	95	0.48	85
	5	0.54	99	0.53	90
	10			0.41	102

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